Seat Number	

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2023 Semester 1 Main Examination

Faculty of Natural Sciences, Department of Chemistry

Qualification:	D. Analytical Chemistry	**Date:**	Fri 2 June 2023
Subject and Level:	Analytical Chemistry II	**Venue:**	NAT SC BLOCK
Subject Code:	ANAC 321/ANCH102	**Time:**	09:00 Hrs
Total Marks:	155	**Duration:**	3 Hours
Full Marks:	150	**Examiners:**	M M Shapi
Annexures:	Periodic table.		F T Zwane
No. of Pgs. incl. cover page:	18	**Moderator:**	N E Damoyi

Student Name: ....

Student's Signature: ....

Student Number: ....

Examiner's Signature: ....

Moderator's Signature: ....

Question	Q1	Q2	Q3	Q4							Total	Full Marks	%
Marks allocated	40	35	37	43							155	145	100%
Examiner													
Moderator													

For office use only:

INSTRUCTIONS TO STUDENTS:

1. Answer all questions in ink.
2. Write all answers in the answer book or question paper provided.
3. Non-programmable calculators may be used.
4. Do not turn over until permission is given.

QUESTIOIN 1: Neutralisation reactions **[40 Marks]**

1.1 A 30.0 cm^3 of 0.020 M solution of NH_3 is titrated with 0.020 M solution of HCl. Calculate the pH of the solution after addition of the following volumes of titrant during titration $K_a = 5.7 \times 10^{-10}$

1.1.1 5.00 cm^3 **(6)**

1.1.2 30.00 cm^3 **(7)**

1.1.3 37.00 cm^3 **(4)**

1.2 With reasonable argument, predict whether the following solutions are acidic, neutral or basic. $K_{aNH4}{}^{+} = 5.7 \times 10^{-10}$, $K_{aHOAc} = 1.75 \times 10^{-10}$, $K_w = 1.0 \times 10^{-14}$

1.2.1 0.100 M NaCl. **(2)**

1.2.2 0.100 M NH_4OAc **(3)**

1.2.3 0.100 M NaOAc **(3)**

1.3 A buffer solution is 0,200 M in acetic acid (HOAc) and in sodium acetate. Calculate the pH change upon addition of 1.0 cm^3 of 0.100 M HCl to 10.0 cm^3 of this buffer solution.

(9)

1.4 Calculate the pH of a solution that is made up of 0.0600 M Na_2CO_3 and 0.030 M $NaHCO_3$. $K_{a2} = 4.69 \times 10^{-11}$. **(6)**

QUESTION 2: Complex Formation Titrations **[35 Marks]**

2.1 A solution containing a zinc ion was treated with EDTA at pH 6.0 ($\alpha_4 = 2.2 \times 10^{-5}$, $K_{MY} = 3.2 \times 10^{16}$). If the concentration of ZnY^{2-} was afterwards found to be 1.25×10^{-2} M, calculate the concentration of Zn^{2+} remaining uncomplexed. **(5)**

2.2 A solution contains 1.694 mg of $CoSO_4$ per millilitre. Calculate the volume of 0.008640 M EDTA needed to titrate the Zn^{2+} displaced by Co^{2+} following addition of an unmeasured excess of ZnY^{2-} to a 25.00 cm^3 aliquot of the $CoSO_4$ solution. The reaction is: $\boldsymbol{Co^{2+} + ZnY^{2-} \rightarrow CoY^{2-} + Zn^{2+}}$. (7)

2.3 The cadmium and lead ions in a 50 cm^3 sample required 40.09 cm^3 of 0.004780 M EDTA for titration. A 75 cm^3 portion of the same sample was made basic and treated with excess KCN, masking cadmium as $Cd(CN)_4^{2-}$. This solution required 31.44 cm^3 of the EDTA for titration. Calculate the concentration of Cd^{2+} and Pb^{2+} in the sample in parts per million.

(13)

2.4 A 25.0 cm^3 aliquot of 0.015 M $Mg(NO_3)_2$ was titrated with 0.010 M EDTA at pH 10 (α_4 – 0.35; $K_{MgY} = 4.9 \times 10^8$). Calculate the pMg^{2+} after addition of 45.00 cm^3 of EDTA.

(10)

QUESTION 3: Precipitation titrations. **[37 Marks]**

3.1 Distinguish between three precipitation methods. **(6)**

3.2 The Volhard method for determination employs the use of nitrobenzene. With the aid of equations explain why nitrobenzene is used. **(3)**

3.3 Write all the equations for the reactions taking place in the Volhard method including the reaction that is responsible for the red colour that is observed when Fe(III) is used as an indicator. **(3)**

3.4 The action of alkaline I_2 solution upon the rodenticide warfarin, $C_{19}H_{16}O_4$, results in the formation of 1 mole of iodoform, CHI_3, for each mole of the parent compound reacted. Analysis of warfarin can then be based upon the reaction between CHI_3 and Ag^+:

$$CHI_3 + 3Ag^+ + H_2O \rightarrow 3AgI + 3H^+ + CO$$

The CHI_3 produced from a 13.96 g sample was treated 25 cm^3 of 0.02979 M $AgNO_3$ and excess Ag^+ was titrated with 2.85 cm^3 of 0.05411 M KSCN. Calculate the percentage of warfarin in the sample. **(10)**

3.5 Calculate the pAg in the titration of 50 cm^3 of 0.050 M KI with 0.100 M $AgNO_3$ after addition of (i) 10 cm^3, (ii) 25 cm^3 and (ii) 30 cm^3. $AgI_{ksp} = 8.3 \times 10^{-17}$. **(15)**

QUESTION 4: Electrochemistry [43 Marks]

4.1. An electrochemical cell contains a Thorium electrode setting in 1.00 M solution of Th^{4+} and a Galium electrode setting in a 1.00 M solution of Ga^{3+}.

$$\mathbf{Th^{4+} + 4e^- \rightleftarrows Th \qquad E^\circ = -1.899\ V}$$

$$\mathbf{Ga^{3+} + 3e^- \rightleftarrows Ga \qquad E^\circ = -0.560\ V}$$

4.1.1 Balance the overall **spontaneous** cell reaction. **(3)**

4.1.2 What is E° for this cell? **(2)**

4.1.3 What is the oxidizing agent of the reaction? **(2)**

4.1.4 What is the equilibrium constant (**K_{eq}**) for this reaction? **(4)**

4.2. Calculato (**against a SHE**) the potential of a mercury (II) electrode in a solution of black mercury sulfide, HgS which contains 4.54 x 10^{-15} M S^{2-}, given that: **(5)**

K_{sp} for IIgS = **6.44 x 10^{-53}**

Hg^{2+} + $2e^-$ $\rightleftarrows$ Hg^0 **E^o = 0.851 V**

4.3 Membrane electrodes are specific to given ions but may be subject to interferences by other ions that may be present in the analysis solutions:

4.3.1 With the help of a suitable schematic diagram explain how the calcium (Ca^{2+}) liquid membrane electrode functions. **(4)**

4.3.2 The Ca^{2+} liquid membrane electrode is vulnerable to interferences by the presences of certain ions in an analysis sample. Name two (2) such ions that can cause major interferences. **(2)**

4.4 For the below unknown metal you are provided with the following data (measured against a Standard Hydrogen Electrode (SHE)):

$$\mathbf{M^{n+} \quad + \quad ne^{-} \quad \rightleftarrows \quad M^{0} \qquad E^{o} = ?\ V}$$

Solution number	**Concentration in Mol/L**	**E (in volts)**
1	1.00×10^{-6}	-0.6246
2	1.00×10^{-5}	-0.5950
3	1.00×10^{-4}	-0.5654
4	1.00×10^{-3}	-0.5358

4.4.1 Plot a graph of $-\log [M^{n+}]$ (on the X-axis) against $-E$ (on Y-axis) on the provided graph paper. The following graph scales are recommended: **(4)**

X-axis: 2 cm = 1; starting from the bottom left hand corner.

Y-axis: 4 cm = 0.1; starting from the bottom left hand corner.

4.4.2 Use the graph in **4.4.1** to determine the number, n, of electrons in the above half reaction for the metal? **(3)**

4.4.3 Determine $\mathbf{E^{o}}$ for the half reaction from your graph. **(3)**

4.4.4 Identify the metal ion in the half reaction using the table provided, giving two (2) reasons for your choice. **(3)**

Table 2 (continued)
REDUCTION REACTIONS HAVING E° VALUES MORE POSITIVE THAN THAT OF THE STANDARD HYDROGEN ELECTRODE

Reaction	E°, V	Reaction	E°, V
$2\,NO + 2\,H^+ + 2\,e \rightleftharpoons N_2O + H_2O$	1.591	$N_2O + 2\,H^+ + 2\,e \rightleftharpoons N_2 + H_2O$	1.766
$Bi_2O_4 + 4\,H^+ + 2\,e \rightleftharpoons 2\,BiO^+ + 2\,H_2O$	1.593	$H_2O_2 + 2\,H^+ + 2\,e \rightleftharpoons 2\,H_2O$	1.776
$HBrO + H^+ + e \rightleftharpoons 1/2\,Br_2(\ell) + H_2O$	1.596	$Co^{3+} + e \rightleftharpoons Co^{2+}$(2 mol/ℓ H_2SO_4)	1.83
$H_5IO_6 + H^+ + 2\,e \rightleftharpoons IO_3^- + 3\,H_2O$	1.601	$Ag^{2+} + e \rightleftharpoons Ag^+$	1.980
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$	1.61	$S_2O_8^{2-} + 2\,e \rightleftharpoons 2\,SO_4^{2-}$	2.010
$HClO + H^+ + e \rightleftharpoons 1/2Cl_2 + H_2O$	1.611	$OH + e \rightleftharpoons OH^-$	2.02
$HClO_2 + 3\,H^+ + 3\,e \rightleftharpoons 1/2Cl_2 + 2\,H_2O$	1.628	$O_3 + 2\,H^+ + 2\,e \rightleftharpoons O_2 + H_2O$	2.076
$HClO_2 + 2\,H^+ + 2\,e \rightleftharpoons HClO + H_2O$	1.645	$S_2O_8^{2-} + 2\,H^+ + 2\,e \rightleftharpoons 2\,HSO_4^-$	2.123
$NiO_2 + 4\,H^+ + 2\,e \rightleftharpoons Ni^{2+} + 2\,H_2O$	1.678	$F_2O + 2\,H^+ + 4\,e \rightleftharpoons H_2O + 2\,F^-$	2.153
$MnO_4^- + 4\,H^+ + 3\,e \rightleftharpoons MnO_2 + 2\,H_2O$	1.679	$FeO_4^{2-} + 8\,H^+ + 3\,e \rightleftharpoons Fe^{3+} + 4\,H_2O$	2.20
$PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e \rightleftharpoons PbSO_4 + 2\,H_2O$	1.6913	$O(g) + 2\,H^+ + 2\,e \rightleftharpoons H_2O$	2.421
$Au^+ + e \rightleftharpoons Au$	1.692	$H_2N_2O_2 + 2\,H^+ + 2\,e \rightleftharpoons N_2 + 2\,H_2O$	2.65
$CeOH^{3+} + H^+ + e \rightleftharpoons Ce^{3+} + H_2O$	1.715	$F_2 + 2\,e \rightleftharpoons 2\,F^-$	2.866
		$F_2 + 2\,H^+ + 2\,e \rightleftharpoons 2\,HF$	3.053

Table 3
REDUCTION REACTIONS HAVING E° VALUES MORE NEGATIVE THAN THAT OF THE STANDARD HYDROGEN ELECTRODE

Reaction	E°, V	Reaction	E°, V
$2\,H^+ + 2\,e \rightleftharpoons H_2$	0.00000	$PbCl_2 + 2\,e \rightleftharpoons Pb + 2\,Cl^-$	−0.2675
$AgCN + e \rightleftharpoons Ag + CN^-$	−0.017	$H_3PO_4 + 2\,H^+ + 2\,e \rightleftharpoons H_3PO_3 + H_2O$	−0.276
$2\,WO_3 + 2\,H^+ + 2\,e \rightleftharpoons W_2O_5 + H_2O$	−0.029	$Co^{2+} + 2\,e \rightleftharpoons Co$	−0.28
$W_2O_5 + 2\,H^+ + 2\,e \rightleftharpoons 2\,WO_2 + H_2O$	−0.031	$PbBr_2 + 2\,e \rightleftharpoons Pb + 2\,Br^-$	−0.284
$D^+ + e \rightleftharpoons 1/2D_2$	−0.0034	$Tl^+ + e \rightleftharpoons Tl(Hg)$	−0.3338
$Ag_2S + 2\,H^+ + 2\,e \rightleftharpoons 2\,Ag + H_2S$	−0.0366	$Tl^+ + e \rightleftharpoons Tl$	−0.336
$Fe^{3+} + 3\,e \rightleftharpoons Fe$	−0.037	$In^{3+} + 3\,e \rightleftharpoons In$	−0.3382
$Hg_2I_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,I^-$	−0.0405	$TlOH + e \rightleftharpoons Tl + OH^-$	−0.34
$2\,D^+ + 2\,e \rightleftharpoons D_2$	−0.044	$PbF_2 + 2\,e \rightleftharpoons Pb + 2\,F^-$	−0.3444
$Tl(OH)_3 + 2\,e \rightleftharpoons TlOH + 2\,OH^-$	−0.05	$PbSO_4 + 2\,e \rightleftharpoons Pb(Hg) + SO_4^{2-}$	−0.3505
$TiOH^{3+} + H^+ + e \rightleftharpoons Ti^{3+} + H_2O$	−0.055	$Cd^{2+} + 2\,e \rightleftharpoons Cd(Hg)$	−0.3521
$2\,H_2SO_3 + H^+ + 2\,e \rightleftharpoons HS_2O_4^- + 2\,H_2O$	−0.056	$PbSO_4 + 2\,e \rightleftharpoons Pb + SO_4^{2-}$	−0.3588
$P(white) + 3\,H^+ + 3\,e \rightleftharpoons PH_3(g)$	−0.063	$Cu_2O + H_2O + 2\,e \rightleftharpoons 2\,Cu + 2\,OH^-$	−0.360
$O_2^- + H_2O + 2\,e \rightleftharpoons HO_2^- + OH^-$	−0.076	$Eu^{3+} + e \rightleftharpoons Eu^{2+}$	−0.36
$2\,Cu(OH)_2 + 2\,e \rightleftharpoons Cu_2O + 2\,OH^- + H_2O$	−0.080	$PbI_2 + 2\,e \rightleftharpoons Pb + 2\,I^-$	−0.365
$WO_3 + 6\,H^+ + 6\,e \rightleftharpoons W + 3\,H_2O$	−0.090	$SeO_3^{2-} + 3\,H_2O + 4\,e \rightleftharpoons Se + 6\,OH^-$	−0.366
$P(red) + 3\,H^+ + 3\,e \rightleftharpoons PH_3(g)$	−0.111	$Ti^{3+} + e \rightleftharpoons Ti^{2+}$	−0.368
$GeO_2 + 2\,H^+ + 2\,e \rightleftharpoons GeO + H_2O$	−0.118	$Se + 2\,H^+ + 2\,e \rightleftharpoons H_2Se(aq)$	−0.399
$WO_2 + 4\,H^+ + 4\,e \rightleftharpoons W + 2\,H_2O$	−0.119	$In^{2+} + e \rightleftharpoons In^+$	−0.40
$Pb^{2+} + 2\,e \rightleftharpoons Pb(Hg)$	−0.1205	$Cd^{2+} + 2\,e \rightleftharpoons Cd$	−0.4030
$Pb^{2+} + 2\,e \rightleftharpoons Pb$	−0.1262	$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	−0.407
$CrO_4^{2-} + 4\,H_2O + 3\,e \rightleftharpoons Cr(OH)_3 + 5\,OH^-$	−0.13	$2\,S + 2\,e \rightleftharpoons S_2^{2-}$	−0.42836
$Sn^{2+} + 2\,e \rightleftharpoons Sn$	−0.1375	$Tl_2SO_4 + 2\,e \rightleftharpoons Tl + SO_4^{2-}$	−0.4360
$In^+ + e \rightleftharpoons In$	−0.14	$In^{3+} + 2\,e \rightleftharpoons In^+$	−0.443
$O_2 + 2\,H_2O + 2\,e \rightleftharpoons H_2O_2 + 2\,OH^-$	−0.146	$Fe^{2+} + 2\,e \rightleftharpoons Fe$	−0.447
$AgI + e \rightleftharpoons Ag + I^-$	−0.15224	$H_3PO_3 + 3\,H^+ + 3\,e \rightleftharpoons P + 3\,H_2O$	−0.454
$2\,NO_2^- + 2\,H_2O + 4\,e \rightleftharpoons N_2O_2^{2-} + 4\,OH^-$	−0.18	$Bi_2O_3 + 3\,H_2O + 6\,e \rightleftharpoons 2\,Bi + 6\,OH^-$	−0.46
$H_2GeO_3 + 4\,H^+ + 4\,e \rightleftharpoons Ge + 3\,H_2O$	−0.182	$NO_2^- + H_2O + e \rightleftharpoons NO + 2\,OH$	−0.46
$CO_2 + 2\,H^+ + 2\,e \rightleftharpoons HCOOH$	−0.199	$PbHPO_4 + 2\,e \rightleftharpoons Pb + HPO_4^{2-}$	−0.465
$Mo^{3+} + 3\,e \rightleftharpoons Mo$	−0.200	$S + 2\,e \rightleftharpoons S^{2-}$	−0.47627
$2\,SO_3^{2-} + 4\,H^+ + 2\,e \rightleftharpoons S_2O_6^{2-} + H_2O$	−0.22	$S + H_2O + 2\,e \rightleftharpoons HS^- + OH^-$	−0.478
$Cu(OH)_2 + 2\,e \rightleftharpoons Cu + 2\,OH^-$	−0.222	$NiO_2 + 2\,H_2O + 2\,e \rightleftharpoons Ni\,(OH)_2 + 2\,OH^-$	−0.490
$CdSO_4 + 2\,e \rightleftharpoons Cd + SO_4^{2-}$	−0.246	$In^{3+} + e \rightleftharpoons In^{2+}$	−0.49
$V(OH)_4^+ + 4\,H^+ + 5\,e \rightleftharpoons V + 4\,H_2O$	−0.254	$H_3PO_3 + 2\,H^+ + 2\,e \rightleftharpoons H_3PO_2 + H_2O$	−0.499
$V^{3+} + e \rightleftharpoons V^{2+}$	−0.255	$TiO_2 + 4\,H^+ + 2\,e \rightleftharpoons Ti^{2+} + 2\,H_2O$	−0.502
$Ni^{2+} + 2\,e \rightleftharpoons Ni$	−0.257	$H_3PO_2 + H^+ + e \rightleftharpoons P + 2\,H_2O$	−0.508

4.5 A nickel indicating electrode is placed in an unknown Ni^{2+} solution and measured against a Standard Hydrogen Electrode (SHE). Given that:

$$\mathbf{Ni^{2+} + 2e^{-} \rightleftarrows Ni^{0}} \qquad \mathbf{E^{o} = -0.257\ V}$$

4.5.1 Calculate the concentration of Ni^{2+} in the unknown solution in mol/L if the measured voltage is -0.427 V. **(4)**

4.5.2 Indicating electrodes actually measure ion activities rather than concentrations. State two conditions under which the activity of ion equals to its concentration. **(2)**

The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	……								

s block | d block | p block

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 256.1	102 No 259.1	103 Lr 260.1

f block